Process of preparing Glycolaldehyde

The present invention relates to a process of
preparing glycolaldehyde and a process of preparing
ethylene glycol from the glycolaldehyde thus prepared.

The reaction of an unsaturated substrate with carbon
5   monoxide and hydrogen is known as hydroformylation. It
has been disclosed in the past that glycolaldehyde, which
is a useful intermediate for the preparation of ethylene
glycol, may be prepared by a hydroformylation reaction of
formaldehyde employing a rhodium catalyst. However, the
10   preparation of glycolaldehyde in this way is hindered in
that the rhodium catalyst also promotes hydrogenation of
formaldehyde to methanol, lowering glycolaldehyde yields.

Attempts have been made to suppress methanol
production and increase selectivity to the glycolaldehyde
15   product and in this regard it has been found that good
yields of glycolaldehyde can be achieved by use of
rhodium catalysts containing aryl-substituted phosphine
ligands such as triphenylphosphine, optionally in
combination with protonoic acids (e.g. see *Pure&Appl.*
20   *Chem.*, Vol. 62, No. 4, pp. 661-669, 1990). However, such
aryl-substituted ligands suffer from the disadvantage
that they are unstable in the reaction conditions,
lessening their effectiveness.

A further limitation on this method of preparing
25   glycolaldehyde, in particular when it is to be used as an
intermediate in the preparation of ethylene glycol, is
that good results are only obtained when using para-
formaldehyde in non-aqueous conditions and that use of
the cheaper aqueous formaldehyde (formaline) gives lower
30   conversion and selectivity to glycolaldehyde. This is
thought to be due to the instability of the catalyst in

aqueous conditions. Indeed, the difficulty in
hydroformylating aqueous formaldehyde represents a major
obstacle to the commercialisation of this approach for
the production of ethylene glycol.

European patent application EP-A-0331512 reviews the
use of a rhodium-phosphine ligand complex, wherein the
phoshine ligand is a triorganophoshine, in the
hydroformylation of aqueous formaldehyde to
glycolaldehyde, which can then be used to prepare
ethylene glycol.

A process has now been developed for hydroformylating
formaldehyde that is based on the use of a rhodium
catalyst and a specific form of phosphine ligand. The
process has performance advantages when compared to known
rhodium catalysts having aryl-substituted phosphine
ligands. Moreover, the catalysts of the present invention
are more stable in aqueous conditions than catalysts
containing aryl-substituted phosphine ligands, and may
readily be used to convert aqueous formaldehyde to
glycolaldehyde.

The present invention provides a process of preparing
glycolaldehyde which comprises reacting formaldehyde with
hydrogen and carbon monoxide in the presence of a
catalyst composition which is based on

   a) a source of rhodium, and
   b) a ligand of general formula

$$R^1P-R^2 \qquad (I)$$

wherein R^1 is a bivalent radical that together with the
phosphorous atom to which it is attached is an optionally
substituted 2-phospha-tricyclo[3.3.1.1{3,7}]-decyl group,
wherein from 1 to 5 of the carbon atoms has been replaced
by a heteroatom, and wherein R^2 is a monovalent radical

which is an optionally substituted hydrocarbyl group
having from 1 to 40 carbon atoms.

The catalyst composition of the present invention
requires a source of rhodium. Convenient sources of
rhodium include rhodium salts of mineral acids, such as
salts of sulphuric acid, nitric acid and phosphoric acid;
salts of sulphonic acids, such as methane sulphonic acid
and para-toluenesulphonic acid; and salts of carboxylic
acids, in particular those having up to 6 carbon atoms,
such as acetic acid, propionic acid and trifluoracetic
acid. Alternatively, the source of rhodium may contain
rhodium in a zero-valent form, complexed by ligands such
as carbon monoxide, acetylacetonates and phosphine
ligands. The source of rhodium metal may contain a
mixture of anions and uncharged ligands, e.g. as in
$Rh.Cl(CO)_2$ or $Rh(acac)(CO)_2$.

In the ligand of general formula (I), R^1 represents a
bivalent radical that together with the phosphorus atom
to which it is attached is an optionally substituted
2-phospha-tricyclo[3.3.1.1{3,7}]decyl group, wherein from
1 to 5 of the carbon atoms has been replaced by a
heteroatom.

Tricyclo[3.3.1.1{3,7}]decane is the systematic name
for a compound more commonly known as adamantane.
Therefore, for ease of reference, in the present
description the optionally substituted 2-phospha-
tricyclo[3.3.1.1{3,7}decyl group, or a derivative
thereof, may be referred to as a "2-PA" group (as in 2-
phosphadamantyl group).

In the ligands employed in the present invention,
from 1 to 5 of the carbon atoms in the "2-PA" group have
been replaced by a heteroatom. Examples of heteroatoms
that may conveniently be used are oxygen and sulphur
atoms, oxygen atoms being preferred. The from 1 to 5

carbon atoms replaced by heteroatoms are preferably those located at positions 4, 6, 8, 9, or 10 of the "2-PA" group. Most preferably 3 carbon atoms of the "2-PA" group have been replaced by heteroatoms, preferably at the 6, 9 and 10 positions.

Preferably, the "2-PA" group is substituted on one or more of the 1, 3, 5 or 7 positions with a monovalent radical of up to 20 atoms, preferably a radical comprising 1 to 10 carbon atoms and more preferably 1 to 6 carbon atoms. Examples of suitable monovalent radicals include methyl, ethyl, propyl, phenyl, and 4-dodecylphenyl groups, methyl and ethyl groups being preferred. More preferably, the "2-PA" group is substituted on each of the 1, 3, 5 and 7 positions. Most preferably the substituents on each of the 1, 3, 5 and 7 positions are identical.

Ligands that have given particularly good results in the present invention are those wherein the bivalent radical R^1 together with the phosphorous atom to which it is attached is a 2-phospha-1,3,5,7-tetralkyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decyl group, as depicted in Figure I: -
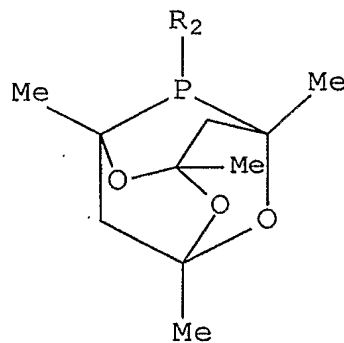

Figure 1.

In the ligand of general formula (I), R^2 is a monovalent radical which is an optionally substituted hydrocarbyl group having from 1 to 40 carbon atoms. The

hydrocarbyl groups may be substituted or unsubstituted,
straight or branched chain, saturated or unsaturated;
preferred such hydrocarbyl groups being alkyl,
cycloalkyl, aryl, alkaryl and aralkyl groups. Where the
hydrocarbyl group is substituted, substituents which the
hydrocarbyl group may conveniently carry may be
independently selected from one or more of halogen atoms
(e.g. fluorine or chlorine), alkoxy, alkenyloxy, aryloxy,
hydroxy, dialkylamido, diarylamido, alkylthio, arylthio,
alkylsuphonyl, alkylsulphinyl, alkoxycarbonyl,
dialkylamino and diarylamino groups. Herein as
substituents suitably an alkyl moiety has from 1 to 4
carbon atoms, an alkenyl moiety has from 2 to 4 carbon
atoms, and an aryl group has from 6 to 12 carbon atoms,
and is especially phenyl. Preferred substituents are
dialkylamido and diarylamido groups.

    In a first preferred embodiment, the process of the
present invention employs a ligand wherein the monovalent
radical R^2 is an alkyl group having in the range of from
4 to 34 carbon atoms. Preferably, the alkyl group R^2 of
this embodiment comprises at least 6 carbon atoms, most
preferably at least 10, especially at least 12, carbon
atoms; and preferably up to 28 carbon atoms, more
preferably up to 22 carbon atoms. The alkyl group may be
linear or branched, however it will preferably be linear.
The ligands of this embodiment are preferred as they
display a high conversion to glycol aldehyde and may
enhance stability of the catalyst. They perform
particularly well in the hydroformylation of formaldehyde
in non-aqueous conditions.

    Ligands that may be conveniently used in the present
invention according to the first preferred embodiment
include 2-phospha-2-hexyl-1,3,5,7-tetramethyl-6,9,10-
trioxa-tricyclo[3.3.1.1{3,7}]-decane, 2-phospha-2-octyl-

1,3,5,7-tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-
decane, 2-phospha-2-dodecyl-1,3,5,7-tetramethyl-6,9,10-
trioxa-tricyclo[3.3.1.1{3,7}]-decane, and 2-phospha-2-
icosyl-1,3,5,7-tetramethyl-6,9,10-trioxa-
tricyclo[3.3.1.1{3,7}]-decane.

In a second preferred embodiment, the process of the
present invention employs a ligand wherein the monovalent
radical R^2 is of general formula

$$-R^3-C(O)NR^4R^5 \quad (II)$$

wherein R^3 is an alkylene group and R^4 and R^5
independently represent an alkyl, cycloalkyl, aryl or
alkaryl group, or R^4 and R^5 together represent a bivalent
bridging group. Conveniently, alkylene group R^3 is a
methylene, ethylene, propylene or butylene group, most
conveniently an ethylene group. Preferably, R^4 and R^5
independently represent an aryl group, for example
phenyl; or an alkyl group, preferably an alkyl group
having from 1 to 22 carbon atoms. Examples of alkyl
groups that may conveniently be used include methyl,
ethyl, propyl, butyl, and pentyl groups. Ligands wherein
R^2 is of general formula (II) are preferred as they
display an excellent conversion to glycolaldehyde and are
particularly advantageous for hydroformylation reactions
performed with aqueous formaldehyde.

Ligands that may be conveniently used in the present
invention according to the second preferred embodiment
include 2-phospha-2-(ethyl-N,N-diethylamido)-1,3,5,7-
tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane,
2-phospha-2-(ethyl-N,N-diphenylamido)-1,3,5,7-
tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane,
and 2-phospha-2-(ethyl-N,N-dimethylamido)-1,3,5,7-
tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane.

The ligands of general formula (I) may be prepared by
coupling an optionally substituted 2-phospha-
tricyclo[3.3.1.1{3,7}]-decane, wherein from 1 to 5 of the
carbon atoms has been replaced by a heteroatom, with a
suitable R^2 group precursor. The 2-phospha-
tricyclo[3.3.1.1{3,7}]-decane may conveniently be
prepared by analogous chemistry to that described in
US-A-3,050,531, wherein for instance 2-phospha-1,3,5,7-
tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane
is prepared by reacting 2,4-pentanedione with phosphine
in the presence of hydrochloric acid. Similar chemistry
is also discussed in chapter 3 of "PRECIOUS METAL
COMPLEXES OF SOME NOVEL FUNCTIONALISED SECONDARY AND
TERTIARY PHOSPHINES" by Ms. Joanne H Downing (thesis
submitted to the University of Bristol on November 1992).

Examples of R^2 group precursors include compounds of
formula R^2-X, wherein X is a halide, for example a
chloride or bromide, which may conveniently be used when
preparing ligands of general formula (I) wherein R^2 is an
alkyl group; for example by reaction of an R^2-X compound
with 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxa-
tricyclo[3.3.1.1{3,7}]-decane or its borane adduct.
Alternatively, when R^2 is of general formula
$-R^3$-C(O)NR^4R^5 (II), the R^2 group precursor may
conveniently be an N,N-disubstituted alkenylamide. For
example, ligands wherein R^3 is an ethylene group and R^4
and R^5 are alkyl groups may be prepared by reaction of a
dialkyl-acrylamide with a "2-PA" group in the presence of
acid, e.g. acetic acid. Other ligands according to the
present invention may be prepared by analogous chemistry,
as will be understood by those skilled in the art.

The catalyst compositions employed in the present
invention may optionally comprise a source of anions c)

as a further catalyst component. Preferred anions are anions of protic acids having a pKa (measured at 18°C in water) of less than 6, preferably less than 4. The anions derived from these acids do not or only weakly co-ordinate with the rhodium, by which it is meant that little or no covalent interaction occurs between the anion and the rhodium. Catalysts comprising such anions exhibit good activity.

Examples of suitable anions include those derived from Bronsted acids, such as phosphoric acid and sulphuric acid; as well as anions derived from sulphonic acids e.g. methanesulphonic acid, trifluoromethane sulphonic acid, p-toluenesulphonic acid and 2,4,6-trimethylbenzenesulphonic acid; and anions derived from carboxylic acids, e.g. 2,4,6-trimethylbenzoic acid, 2,4,6 tri-isopropylbenzoic acid; 9-antracene carboxylic acid and halogenated carboxylic acids such as trifluoroacetic acid 2,6-dichlorobenzoic acid, and 2,6 bis(trifluoromethyl)benzoic acid. Particularly good results have been obtained using alkyl-substituted benzoic acids, especially C_1 to C_4 alkyl-substituted benzoic acids, as a source of anions.

Also suitable are complex anions, such as the anions generated by the combination of a Lewis acid such as BF_3, $B(C_6F_5)_3$, $AlCl_3$, SnF_2, $Sn(CF_3SO_3)_2$, $SnCl_2$ or $GeCl_2$, with a protic acid, preferably having a pKa of less than 5, such as a sulphonic acid, e.g. CF_3SO_3H or CH_3SO_3H or a hydrohalogenic acid such as HF or HCl, or a combination of a Lewis acid with an alcohol. Examples of such complex anions are BF_4^-, $SnCl_3^-$, $[SnCl_2.CF_3SO_3]^-$ and PF_6^-.

The molar ratio of carbon monoxide to hydrogen supplied to the process of the present invention is not critical and may vary over a wide range, for example of

from 5:95 to 95:5, preferably of from 30:70 to 80:20.
However, it is generally preferred to use a gas stream in
which the molar ratio of $CO:H_2$ is at least 1:1, since
this minimises the formation of methanol. The process is
preferably conducted under pressure, conveniently in the
range of from 5 to 200 bar (0.5 to 20 MPa) and preferably
in the range of from 10 to 50 bar (1 to 5 MPa). Higher
pressures may be used, however they are generally
considered uneconomical. Inert gasses may also be present
in the gas stream but as this leads to an increase in
total pressure it is generally undesirable.

The hydroformylation reaction of the present
invention may be conveniently carried out at moderate
temperatures, preferably in the range of from 22 to 180
°C, more preferably 50 to 130 °C. The use of a
temperature as low as possible commensurate with the
desired reaction rate is preferred since at higher
temperatures the glycolaldehyde product is susceptible to
undergo side reactions, e.g. aldol condensation
reactions.

The reaction time for the process of the invention is
of course dependent on the temperature and pressure
conditions utilised. It has been generally found that
the reaction time may be in the range of from 1 to 10
hours, preferably 1 to 6 hours, especially 2 to 5 hours.

The quantity in which the catalyst system is used in
the present invention is not critical and may vary within
wide limits. However, the amount of mole atom of rhodium
metal per mole of formaldehyde will preferably be in the
range of from 1:1 to 1:10^6, more preferably from 1:10 to
1:10^5, and even more preferably from 1:100 to 1:10^4.

For the preparation of catalyst systems employed in
the present invention, the amount of ligand of general
formula (I) is generally applied in an excess to the

amount of rhodium, expressed as moles of ligand per mole
atom of rhodium. Typically the amount of ligand is
selected such that per mole atom of rhodium 1 to 20 moles
of ligand are present. However, for a preferred catalyst
system the molar amount of ligand per mole of rhodium is
preferably in the range of from 2 to 10, more preferably
in the range of from 2 to 5. When present the amount of
the anion source c), whilst not critical, may range from
1 to 500, preferably from 1 to 150, and more preferably
from 1 to 20 moles per mole atom of rhodium.

The process of the present invention may be carried
out in the presence of a solvent. Examples of solvents
that may conveniently be used include nitriles, pyridine,
substituted or unsubstituted ureas, for example
N,N,N',N'-tetrasubstituted ureas, and substituted or
unsubstituted amides, for example N,N-disubstituted
amides.

The formaldehyde may be introduced into the reaction
system in any suitable form, or it may be generated in
situ. A convenient source of formaldehyde is para-
formaldehyde. Further, it is an advantageous feature of
the present invention that good results are achieved when
aqueous formaldehyde is employed as the source of
formaldehyde. Accordingly, in a preferred process
according to the present invention the source of
formaldehyde is aqueous formaldehyde.

Where the source of formaldehyde is aqueous
formaldehyde it is further preferred that the process is
performed in a reaction medium comprising an aqueous
phase and an organic phase, wherein the organic phase and
aqueous phase are immiscible at 22 °C. For the avoidance
of doubt, by immiscible it is meant that on standing at
22 °C the organic phase and aqueous phase will separate
into two distinct layers. A reaction medium comprising an

aqueous phase and an organic phase is preferred as on
completion of the reaction the catalyst will reside in
the organic phase, whilst the glycolaldehyde product will
reside in the aqueous phase, and thus the product may

5   readily be separated from the catalyst by phase
separation. Such an approach is possible in the present
invention as the catalyst compositions are more stable in
aqueous conditions than known catalysts based on aryl-
substituted phosphine ligands.

10   Where the process is performed in a reaction medium
comprising an aqueous phase and an organic phase, the
solvent of the organic phase may conveniently be a water-
immiscible amide solvent. Examples of water-immiscible
amide solvents that can be employed in the present

15   invention are those comprising long chain alkyl moieties
and includes N-alkyl-2-pyrrolidones wherein the alkyl
group comprises at least 7 carbon atoms, preferably in
the range of from 8 to 20 carbon atoms, N,N-dialkyl-
acetamides, in which each alkyl group has in the range of

20   from 1 to 10 carbon atoms, preferably from 1 to 6 carbon
atoms, and N,N-diaryl-acetamides, preferably N,N-
diphenylacetamide. Examples of water-immiscible amide
solvents that have given particularly good results when
employed in the present invention include N-octyl-

25   pyrrolidone and N,N-dibutyl-acetamide.

A particularly preferred embodiment of the present
invention is wherein the process is performed in a
reaction medium comprising an aqueous phase and an
organic phase comprising a water-immiscible amide

30   solvent, and wherein in the ligand of general formula
R^1P-R^2 (I), the monovalent radical R^2 is of general
formula $-R^3-C(O)NR^4R^5$ (II).

The rhodium-containing catalyst compositions described herein above were specifically developed for use in the process of the present invention.

Catalyst compositions of this type fall within the wide-ranging definition of metal-ligand complexes described in US-A-2003/0092935 for the hydroformylation of olefins such as α-olefins, internal olefins, and internal branched olefins. The preferred catalyst compositions for use in the process of the present invention are distant from the preferred metal-ligand complexes of US-A-2003/0092935 and display an excellent activity in the hydroformylation of formaldehyde, a very different substrate, in both non-aqueous and aqueous conditions. Catalyst compositions in which the monovalent radical R^2, of the ligand (I), is of general formula $-R^3-C(O)NR^4R^5$ (II) perform especially well in aqueous conditions for example when formalin is used as the substrate, or when water is present in the reaction medium. Accordingly, the present invention further provides a catalyst composition obtainable by combining a) a source of rhodium, b) a ligand of general formula

$$R^1P-R^2 \qquad (I)$$

wherein R^1 is a bivalent radical that together with the phosphorous atom to which it is attached is an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]-decyl group, wherein from 1 to 5 of the carbon atoms has been replaced by a heteroatom, and wherein R^2 is a monovalent radical which is an optionally substituted alkyl group having from 10 to 40 carbon atoms, or is, preferably, of the general formula $-R^3-C(O)NR^4R^5$, wherein R^3 is an alkylene group and R^4 and R^5 independently represent an alkyl,

cycloalkyl, aryl or alkaryl group or R^4 and R^5 together represent a bivalent bridging group,
and optionally c) a source of anions. Within these definitions of R^2, preferred catalyst compositions as described herein before with respect to the process of the present invention are similarly preferred as the catalyst composition of the invention.

An important use of glycolaldehyde is its conversion to ethylene glycol and the present invention still further provides a process of preparing ethylene glycol by hydrogenating glycolaldehyde prepared by the hydroformylation process described herein above.

Hydrogenation catalysts of use in the conversion of glycolaldehyde to ethylene glycol are well known in the art, for example palladium, platinum or nickel catalysts, often in heterogeneous form. Where glycolaldehyde is prepared in non-aqueous conditions, the selected hydrogenation catalyst may be added directly to the reaction mixture resulting from the preparation of glycolaldehyde with no work-up procedure, and gaseous hydrogen introduced. Alternatively, the reaction mixture may be worked-up before the glycolaldehyde is hydrogenated, e.g. by extraction with a suitable solvent such as water or ethylene glycol itself, and the resulting solution then hydrogenated in conventional manner. This approach is particularly convenient when the glycolaldehyde is prepared from aqueous formaldehyde in a reaction medium comprising an aqueous phase as has now been made possible by means of the present invention.

The invention will be further understood from the following illustrative examples.

Ligand Synthesis

The following examples, which were performed under an atmosphere of purified argon using standard Schlenk techniques, illustrate a typical preparation of a ligand according to the present invention wherein (i) R^2 is an alkyl group (2-phospha-2-icosyl-1,3,5,7-tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane), and (ii) R^2 is of general formula (II) (2-phospha-2-(ethyl-N,N-dimethylamido)-1,3,5,7-tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane).

(i) Synthesis of 2-phospha-2-icosyl-1,3,5,7-tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane.

A borane adduct of 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane was prepared by adding BH_3.THF (70 ml of 1M solution in THF) to a solution of 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane (60 mmol) in THF at 0°C. The reaction mixture was allowed to warm to room temperature and stir for two hours after which time the solvent was removed in vacuo to yield the borane adduct.

To a solution of this adduct (16 mmol in THF) a solution of hexyl-lithium (6.4 ml, 2.5M in hexane) was added at a temperature of – 70 °C and the reaction mixture allowed to slowly warm to – 20 °C over a period of 1 hour. After recooling to – 70 °C, a solution of 1-bromo-icosane (16 mmol in THF) was added. The reaction mixture was then allowed to warm to ambient temperature and stirred for 2 hours before diethylamine (3 ml) was added and the reaction mixture then refluxed for 12 hours. On completion of the reaction the solvent was removed in vacuo. The product was then isolated by solvent extraction in dichloromethane-toluene and water, the toluene fractions being evaporated to leave a solid

residue that was washed with methanol to yield 2-phospha-2-icosyl-1,3,5,7-tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane (96 %).

(ii) Synthesis of 2-phospha-2-(ethyl-N,N-dimethylamido)-1,3,5,7-tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane.

2-Phospha-1,3,5,7-tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane (40 mmol) and N,N dimethylacrylamide (100 mmol) were introduced into a Schlenk-tube containing a mixture of toluene and acetic acid, and heated to a temperature of 115 °C. After 18 hours the reaction mixture was cooled to 80 °C and the solvents evaporated *in vacuo*. The residue was then dissolved in triethylamine and the mixture heated to a temperature of 100 °C for 2.5 hours after which the resulting homogeneous mixture was cooled to ambient temperature. The product was then isolated by solvent extraction with toluene and water, the toluene fractions being evaporated to yield 2-phospha-2-(ethyl-N,N-dimethylamido)-1,3,5,7-tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane (79 %).

Hydroformylation of formaldehyde

The following examples were performed in a magnetically stirred 250 ml autoclave. The autoclave was charged with reactants and solvent after which air was removed and the autoclave pressurised with carbon monoxide and hydrogen, each to a partial pressure of 30bar (3MPa). The contents of the autoclave were then heated to reaction temperature. Upon completion of the reaction, the contents were cooled and the conversion of formaldehyde, and yield of glycolaldehyde, was determined by means of gas-liquid chromatography using di-ethylene

glycol dimethylether as an internal standard. All ligands were prepared using analogous chemistry to that described for ligands (i) and (ii) above.

Example 1

("2-PA"-C_{20} ligand in non-aqueous conditions)

The autoclave was charged with 0.17 mol of formaldehyde, in the form of para-formaldehyde, 62 ml (0.58 mol) of N-methyl-pyrrolidone, 0.25 mmol of rhodiumdicarbonylacetonylacetone (Rh(acac)(CO)$_2$), 0.50 mmol of 2-phospha-2-icosyl-1,3,5,7-tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane, and 9.1 mmol of trimethylbenzoic acid. The contents of the autoclave were then heated to a temperature of 110 °C and maintained at that temperature for 2 hours.

Conversion of formaldehyde was 100% and the yield of glycolaldehyde, calculated on formaldehyde intake, was 76%. The initial reaction rate was calculated by measurement of the pressure drop to be 595 mol CO/mol Rh.h.

Example 2

("2-PA"-C_{20} ligand in aqueous conditions)

The autoclave was charged with 0.17 mol of formaldehyde, in the form of para-formaldehyde, 35 ml (0.22 mol) of dibutyl-acetamide, 25 ml of demineralised water, 0.25 mmol of Rh(acac)(CO)$_2$, 0.53 mmol of 2-phospha-2-icosyl-1,3,5,7-tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane, and 9.1 mmol of trimethylbenzoic acid. The contents of the autoclave were heated to a temperature of 110 °C and maintained at that temperature for 5 hours.

Conversion of formaldehyde was 64 % and the yield of glycolaldehyde in the two-phase reaction product, calculated on formaldehyde intake, was 45 %. The initial

reaction rate was calculated by measurement of the
pressure drop to be 115 mol CO/mol Rh.h

Example 3

("2-PA"-CH2CH2C(O)NMe2 ligand in non-aqueous conditions)

The autoclave was charged with 0.18 mol of
formaldehyde, in the form of para-formaldehyde, 23 ml
(0.15 mol) of di-sec-butyl-acetamide, 0.25 mmol of
Rh(acac)(CO)2, 0.49 mmol of 2-phospha-2-(ethyl-N,N-
dimethylamido)-1,3,5,7-tetramethyl-6,9,10-trioxa-
tricyclo[3.3.1.1{3,7}]-decane, and 9.1 mmol of
trimethylbenzoic acid. The contents of the autoclave were
then heated to a temperature of 100 °C and maintained at
that temperature for 3 hours.

Conversion of formaldehyde was 72 % and the yield of
glycolaldehyde in the single-phase reaction product,
calculated on formaldehyde intake, was 69 %. The initial
reaction rate was calculated by measurement of the
pressure drop to be 275 mol CO/mol Rh.h.

Example 4

("2-PA"-CH2CH2C(O)NMe2 ligand in non-aqueous conditions)

The autoclave was charged with 0.25 mol of
formaldehyde, in the form of para-formaldehyde, 35 ml
(0.26 mol) of N,N'-dimethylpropylenurea, 0.10 mmol of
Rh(acac)(CO)2, 0.20 mmol of 2-phospha-2-(ethyl-N,N-
dimethylamido)-1,3,5,7-tetramethyl-6,9,10-trioxa-
tricyclo[3.3.1.1{3,7}]-decane, and 3.1 mmol of
trimethylbenzoic acid. The contents of the autoclave were
then heated to a temperature of 90 °C and maintained at
that temperature for 5 hours.

Conversion of formaldehyde was 73 % and the yield of
glycolaldehyde in the single-phase reaction product,
calculated on formaldehyde intake, was 71 %. The initial

reaction rate was calculated by measurement of the pressure drop to be 595 mol CO/mol Rh.h.

Example 5

("2-PA"-$CH_2CH_2C_{18}$ ligand in non-aqueous conditions)

The autoclave was charged with 0.25 mol of formaldehyde, in the form of para-formaldehyde, 35 ml (0.26 mol) of N,N'-dimethylpropylenurea, 0.10 mmol of Rh(acac)(CO)$_2$, 0.20 mmol of 2-phospha-2-octyl-1,3,5,7-tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane, and 3.1 mmol of trimethylbenzoic acid. The contents of the autoclave were then heated to a temperature of 90 °C and maintained at that temperature for 5 hours.

Conversion of formaldehyde was 69 % and the yield of glycolaldehyde in the single-phase reaction product, calculated on formaldehyde intake, was 66 %. The initial reaction rate was calculated by measurement of the pressure drop to be 518 mol CO/mol Rh.h.

Example 6

("2-PA"-$CH_2CH_2C(O)NMe_2$ ligand in aqueous conditions)

The autoclave was charged with 0.15 mol of formaldehyde, in the form of a formaline solution (37 % formaldehyde in water), 37 ml (0.22 mol) of dibutyl-acetamide, 7.5 ml of demineralised water, 0.49 mmol of Rh(acac)(CO)$_2$, 0.96 mmol of 2-phospha-2-(ethyl-N,N-dimethylamido)-1,3,5,7-tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-decane, and 9.1 mmol of trimethylbenzoic acid. The contents of the autoclave were heated to a temperature of 90 °C and maintained at that temperature for 5 hours.

Conversion of formaldehyde was 90 % and the yield of glycolaldehyde in the two-phase reaction product, calculated on formaldehyde intake, was 90 %. The initial

reaction rate was calculated by measurement of the
pressure drop to be 170 mol CO/mol Rh.h.

Example 7

("2-PA"- $CH_2CH_2C(O)NPh_2$ ligand in aqueous conditions)

The autoclave was charged with 0.15 mol of
formaldehyde, in the form of a formaline solution (37 %
formaldehyde), 37 ml (0.22 mol) of dibutyl-acetamide, 7.5
ml of demineralised water, 0.44 mmol of Rh(acac)(CO)$_2$,
0.89 mmol of 2-phospha-2-(ethyl-N,N-diphenylamido)-
1,3,5,7-tetramethyl-6,9,10-trioxa-tricyclo[3.3.1.1{3,7}]-
decane, and 9.1 mmol of trimethylbenzoic acid. The
contents of the autoclave were heated to a temperature of
110 °C and maintained at that temperature for 3 hours.

Conversion of formaldehyde was 100 % and the yield of
glycolaldehyde in the two-phase reaction product,
calculated on formaldehyde intake, was 52 %. The initial
reaction rate was calculated by measurement of the
pressure drop to be 180 mol CO/mol Rh.h.

Comparative Example A

(PPh$_3$ ligand in non-aqueous conditions)

The autoclave was charged with 0.17 mol of
formaldehyde, in the form of para-formaldehyde, 37 ml
(0.24 mol) of dibutyl-acetamide, 0.25 mmol of
Rh(acac)(CO)$_2$, 0.52 mmol of triphenylphosphine, and 9.3
mmol of trimethylbenzoic acid. The contents of the
autoclave were then heated to a temperature of 90 °C and
maintained at that temperature for 10 hours.

Conversion of formaldehyde was 61 % and the yield of
glycolaldehyde in the single-phase reaction product,
calculated on formaldehyde intake, was 40 %. The initial
reaction rate was calculated by measurement of the
pressure drop to be 75 mol CO/mol Rh.h

Comparative Example B

(PPh₃ ligand in aqueous conditions)

The autoclave was charged with 0.17 mol of formaldehyde, in the form of para-formaldehyde, 37 ml (0.22 mol) of dibutyl-acetamide, 12.5 ml of demineralised water, 0.25 mmol of Rh(acac)(CO)$_2$, 0.52 mmol of triphenylphosphine, and 9.1 mmol of trimethylbenzoic acid. The contents of the autoclave were heated to a temperature of 90 °C and maintained at that temperature for 10 hours.

Conversion of formaldehyde was 54 % and the yield of glycolaldehyde in the two-phase reaction product, calculated on formaldehyde intake, was 25 %. The reaction rate was calculated by measurement of the pressure drop to be 51 mol CO/mol Rh.h.

Comparative Example C

(9-icosyl-9-phosphabicyclo[3.3.1]nonane ligand in aqueous conditions)

The autoclave was charged with 0.17 mol of formaldehyde, in the form of para-formaldehyde, 37 ml (0.19 mol) of N-octyl-pyrrolidone, 25 ml of demineralised water, 0.25 mmol of Rh(acac)(CO)$_2$, 0.52 mmol of 9-icosyl-9-phosphabicyclo[3.3.1]nonane, and 9.1 mmol of trimethylbenzoic acid. The contents of the autoclave were heated to a temperature of 110 °C and maintained at that temperature for 5 hours.

Conversion of formaldehyde was 17 % and the yield of glycolaldehyde in the two-phase reaction product, calculated on formaldehyde intake, was 6 %.

Comparative Example D

(9-CH$_2$CH$_2$C(O)NMe$_2$-9-phosphabicyclo[3.3.1]nonane ligand in aqueous conditions)

The autoclave was charged with 0.17 mol of
formaldehyde, in the form of para-formaldehyde, 37 ml
(0.22 mol) of dibutyl-acetamide, 25 ml of demineralised
water, 0.25 mmol of Rh(acac)(CO)$_2$, 0.50 mmol of 9-
phospha-9-(ethyl-N,N-dimethylamido-bicyclo[3.3.1]nonane,
and 9.1 mmol of trimethylbenzoic acid. The contents of
the autoclave were then heated to a temperature of 110 °C
and maintained at that temperature for 5 hours.

Conversion of formaldehyde was 3 % and the yield of
glycolaldehyde in the two-phase reaction product,
calculated on formaldehyde intake, was 0 %.

The above examples demonstrate that catalyst
compositions according to the present invention display a
superior performance to comparative compositions
containing a triphenylphosphine ligand under both aqueous
and non-aqueous conditions (e.g. compare Examples 1 and 3
with Comparative Example A, and Examples 2 and 4 with
Comparative Example B), and to catalysts based on other
forms of bicyclic phosphine-containing ligand (see
Comparative Examples C and D). Moreover, from Examples 4
and 5 it can also be seen that catalyst compositions of
general formula (I) wherein R^2 is of general formula
$-R^3-C(O)NR^4R^5$ continue to display a good level of
performance even under aqueous conditions.

Hydrogenation to Ethylene glycol

To demonstrate the ease with which glycolaldehyde
prepared according to the present invention may be
converted to ethylene glycol, an aqueous phase separated
from a hydroformylation reaction performed under
conditions analogous to those of Example 2 ("2-PA"-C$_{20}$
ligand in aqueous conditions) was treated with Raney
Nickel slurry. The aqueous phase (25 ml, 9.5%wt
glycolaldehyde) was mixed with Raney Nickel slurry (2ml)

and stirred for 15 hours at a temperature 40°C, then
treated with hydrogen at a pressure of 50 bar (5Mpa). The
conversion from glycolaldehyde to ethylene glycol was
90%.